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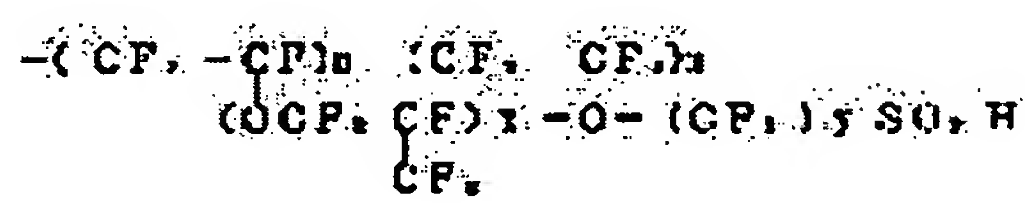
(54) ELECTRODE CATALYST COATING AGENT FOR FUEL CELL AND MEMBRANE/ELECTRODE JOINT BODY USING SAME COATING AGENT

(57)Abstract:



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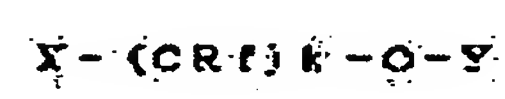

II

PROBLEM TO BE SOLVED: To lower an oxygen-concentration overvoltage when normal-pressure air is supplied and provide a high output voltage, by using a composition comprising a perfluorosulfonic-acid polymer and a fluorine-containing ether compound as an electrode-catalyst coating agent used for a gas diffusion electrode.

SOLUTION: A membrane/electrode joint body for a solid high-polymer type fuel cell comprises an ion-exchange membrane serving as an electrolyte and a gas diffusion electrode jointed to the ion-exchange membrane. An electrode- catalyst coating agent used for the gas diffusion electrode contains a perfluorosulfonic-acid polymer of 30 to 95 wt.% expressed by an expression I and a fluorine-containing ether compound of 5 to 70 wt.% expressed by an expression II. In the expression I, x=0 to 2, y=2 to 3, and n/m=1 to 10. In the expression II, Rf is a perfluoroalkylene group having the C number of 1 to 3, x and y are perfluoroalkyl groups having the C number of 1 to 5, and k is 1 to 100. The gas diffusion electrode using the electrode-catalyst coating agent is used at least on the side of a cathode.

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CLAIMS

[Claim(s)]
[Claim 1] Electrode catalyst coating which consists of a constituent which contains the fluorine-containing ether compound expressed with a general formula (2) 30 to 95% of the weight in the film / electrode zygote for polymer electrolyte fuel cells which consists of ion exchange membrane used as an electrolyte, and a gas diffusion electrode joined to this ion exchange membrane in the perfluoro sulfonic-acid polymer which is used for this gas diffusion electrode, and which is electrode catalyst coating and is expressed with a general formula (1) in 5 - 70% of the weight of the range.
[Formula 1]

$$\begin{array}{l} -(CF_2-\underset{|}{C}F)_m-(CF_2-CF_2)_n- \qquad (1) \\ \qquad (OCF_2\underset{|}{C}F)_x-O-(CF_2)_ySO_3H \\ \qquad\qquad\quad CF_3 \end{array}$$

(Here, it is the integer of x=0-2, the integer of y=2-3, and n/m=1-10.)
[Formula 2]

$$X-(ORf)_k-O-Y \qquad (2)$$

(Here, Rf is X, the perfluoro alkylene group of 1-3 carbon numbers of a single or two or more classes and Y are the perfluoroalkyl radicals of 1-5 carbon numbers, double association may be included, and the radical chosen from H, Cl, Br, SO3 H, and a COOR radical may permute by each carbon to one per each carbon.) R is H or an alkyl group. Moreover, it is the range of k=1-100.
[Claim 2] The film / electrode zygote for polymer electrolyte fuel cells characterized by using the gas diffusion electrode using electrode catalyst coating according to claim 1 for a cathode side at least.

[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] the gas diffusion electrode with which this invention constitutes a polymer electrolyte fuel cell -- business -- **** -- an electrode -- a catalyst -- coating -- it is related and is related with the film / electrode zygote for polymer electrolyte fuel cells which has a gas diffusion electrode using this electrode catalyst coating.
[0002]
[Description of the Prior Art] By oxidizing fuels, such as hydrogen and a methanol, electrochemically within a cell, the chemical energy of a fuel is transformed into direct electrical energy, and a fuel cell takes it out, and attracts attention as a clean electrical energy source of supply in recent years. High power density is obtained, and since low-temperature actuation is possible, the polymer electrolyte fuel cell using especially ion exchange membrane as an electrolyte is expected as a power source for electric vehicles.
[0003] Such basic structure of a polymer electrolyte fuel cell consists of ion exchange membrane which is a solid electrolyte, and a gas diffusion electrode of a pair joined by the both sides, and even if there are few each gas diffusion electrodes, the catalyst is supported at the ion-exchange-membrane side. And it operates as a fuel cell by supplying the oxygen or air which is an oxidizer about the hydrogen which is a fuel at another gas diffusion electrode to one gas diffusion electrode, respectively, and connecting an external load circuit to it among both gas diffusion electrodes. That is, in the former gas diffusion electrode (anode), a proton and an electron arise by oxidation of a fuel, the inside of an electrolyte is conducted, it moves to the latter gas diffusion electrode (cathode), a proton and the oxygen in an oxidizer react here, and this proton generates water. At this time, when the electron produced with the anode moves in an external load circuit and moves to a cathode, electrical energy is obtained.
[0004] In such a polymer electrolyte fuel cell, the proton shift to the catalyst top currently supported by the gas diffusion electrode is carried, it is the purpose which raises the use effectiveness of this catalyst, and the proton conductivity polyelectrolyte is used as electrode catalyst coating. The proton conductivity polyelectrolyte mainly used for current and a polymer electrolyte fuel cell is a perfluoro sulfonic-acid content polymer represented by "Nafion (trademark)" by U.S. Du Pont, "ASHIPU REXX-S (trademark) etc." by Asahi Chemical Industry Co., Ltd., etc. Since these polymers have a strong acid nature machine and it has high chemical stability, it is used as ion exchange membrane as an electrolyte, and also using the solution as electrode catalyst coating of the catalyst bed of a gas diffusion electrode is proposed (for example, JP,2-7398,B, JP,3-208260,A, etc.).
[0005] However, since electrode catalyst coating of the oxygen supply capacity which lets this coating to a catalyst bed pass used conventionally was inadequate, it had the fault that oxygen concentration overvoltage was high. Therefore, when it was going to obtain high output voltage, the means of pressurizing oxygen, or raising concentration and supplying was required, and the system expensive as the whole cell for that purpose was required. Electrode catalyst coating with low oxygen concentration overvoltage by which high output voltage is obtained from this even if it supplies air by ordinary pressure was desired.
[0006]
[Problem(s) to be Solved by the Invention] Since this invention persons had oxygen permeability

with the expensive constituent which consists of a perfluoro sulfonic-acid polymer used conventionally and a fluorine-containing ether compound of a certain kind, they could reduce the oxygen concentration overvoltage when supplying the air of ordinary pressure by using this as electrode catalyst coating, found out that the film / electrode zygote for polymer electrolyte fuel cells with which high output voltage is obtained were obtained, and resulted in this invention.
[0007]
[The means for solving invention] That is, this invention is as follows.
1. Electrode catalyst coating which consists of constituent which contains fluorine-containing ether compound expressed with general formula (2) 30 to 95% of the weight in film / electrode zygote for polymer electrolyte fuel cells which consists of ion exchange membrane used as electrolyte, and gas diffusion electrode joined to this ion exchange membrane in perfluoro sulfonic-acid polymer which is used for this gas diffusion electrode, and which is electrode catalyst coating and is expressed with general formula (1) in 5 - 70% of the weight of range.
[0008]
[Formula 3]

$$-(CF_2-\underset{|}{C}F)_m-(CF_2-CF_2)_n- \qquad (1)$$
$$(OCF_2\underset{\underset{CF_3}{|}}{C}F)_x-O-(CF_2)_y SO_3H$$

(Here, it is the integer of x=0-2, the integer of y=2-3, and n/m=1-10.)
[0009]
[Formula 4]

$$X-(ORf)_k-O-Y \qquad (2)$$

(Here, Rf is X, the perfluoro alkylene group of 1-3 carbon numbers of a single or two or more classes and Y are the perfluoroalkyl radicals of 1-5 carbon numbers, double association may be included, and the radical chosen from H, Cl, Br, SO3 H, and a COOR radical may permute by each carbon to one per each carbon.) R is H or an alkyl group. Moreover, it is the range of k=1-100.
2. Film / electrode zygote for polymer electrolyte fuel cells characterized by using gas diffusion electrode using electrode catalyst coating of the above 1 for cathode side at least.
[0010] About the component of electrode catalyst coating of this invention, sequential explanation is given below. Although the thing of the range of x=0-2 can be first used about the perfluoro sulfonic-acid polymer which has the structure first expressed with a general formula (1), since manufacture and a polymerization are easy, x= 1 is desirable. Moreover, although using in n/m=1-10 is possible, since a high molecular weight object is easy to be acquired and it is easy to dissolve also in a solvent, n/m=2-7 are desirable. Therefore, Du Pont "Nafion", "ASHIPU REXX-S" by Asahi Chemical Industry Co., Ltd., etc. can use the perfluoro sulfonic-acid polymer used from the former as it is.
[0011] Next, the fluorine-containing ether compound expressed with a general formula (2) is explained. In a general formula (2), Rf is the perfluoro alkylene group of 1-3 carbon numbers of a single or two or more classes. It is specifically -CF2-, -CF2 CF2-, -CF2CF2 CF2-, -CF2 CF(CF3)-, etc., and you may mix and have two or more sorts in intramolecular. In these, especially the thing containing -CF2 CF(CF3)- is desirable. Moreover, X and Y are the perfluoroalkyl radicals of 1-5 carbon numbers, and the thing of 1-3 carbon numbers may be desirable, and may include double association. The radical chosen from H, Cl, Br, SO3 H, and a COOR radical may permute by each carbon to per [of one each] each carbon. R is H or an alkyl group and, in the case of an alkyl group, its thing of 1-3 carbon numbers is desirable. Even if X and Y are the same, they may differ. If an example is illustrated, CF3-, CF3 CF2-, CF3 CF2 CF2-, CF3 CHF-, CF2 =CF-, CHF2 CHF-, CClF2 CClF-, CBrF2 CBrF-, HOOCCF2-, CH3 OOCCF2-, Radicals, such as HOOCCF(CF3)-, CH3 OOCCF(CF3)-, HO3 SCF2 CF2-, HO3 SCF2 CF2 CF2-, and HO3 S-CF(CF3) CF2-, are mentioned. Since itis [solution-] easy toize among the compounds which consist of such combination and easy to mix also with a perfluoro sulfonic-acid polymer, the compound which has 1-2 COOH radicals or/and SO3 H set in intramolecular at least is desirable. Specifically, the following compounds can be illustrated.

[0012]
[Formula 5]

$$HOOC-\underset{\overset{|}{CF_3}}{C}F-(OCF_2\underset{\overset{|}{CF_3}}{C}F)k-OCF_2CF_2CF_3$$

$$HOOC-\underset{\overset{|}{CF_3}}{C}F-(OCF_2\underset{\overset{|}{CF_3}}{C}F)k-OCF_2CF_2SO_3H$$

$$HOOC-\underset{\overset{|}{CF_3}}{C}F-(OCF_2\underset{\overset{|}{CF_3}}{C}F)k-OCF_2CF_2CF_2SO_3H$$

$$HOOC-\underset{\overset{|}{CF_3}}{C}F-(OCF_2\underset{\overset{|}{CF_3}}{C}F)k-OCF_2CF_2COOH$$

$$HOOC-\underset{\overset{|}{CF_3}}{C}F-(OCF_2\underset{\overset{|}{CF_3}}{C}F)k-OCF_2\underset{\overset{|}{CF_3}}{C}FSO_3H$$

$$CF_2=CF-(OCF_2\underset{\overset{|}{CF_3}}{C}F)k-OCF_2CF_2SO_3H$$

$$CF_2=CF-(OCF_2\underset{\overset{|}{CF_3}}{C}F)k-OCF_2CF_2CF_2SO_3H$$

$$CF_2=CF-(OCF_2\underset{\overset{|}{CF_3}}{C}F)k-OCF_2CF_2COOH$$

$$CClF_2CClF-(OCF_2\underset{\overset{|}{CF_3}}{C}F)k-OCF_2CF_2SO_3H$$

$$CClF_2CClF-(OCF_2\underset{\overset{|}{CF_3}}{C}F)k-OCF_2CF_2COOH$$

$$CHF_2CHF-(OCF_2\underset{\overset{|}{CF_3}}{C}F)k-OCF_2CF_2SO_3H$$

$$CHF_2CHF-(OCF_2\underset{\overset{|}{CF_3}}{C}F)k-OCF_2CF_2COOH$$

$$CF_3CHF-(OCF_2\underset{\overset{|}{CF_3}}{C}F)k-OCF_2CF_2SO_3H$$

$$CF_3CHF-(OCF_2\underset{\overset{|}{CF_3}}{C}F)k-OCF_2CF_2COOH$$

$$HOOCCF_2-(OCF_2\underset{\overset{|}{CF_3}}{C}F)k1-(OCF_2)k2-OCF_2COOH \quad k1+k2=k$$

$$HOOCCF_2-(OCF_2CF_2)k1-(OCF_2)k2-OCF_2COOH \quad k1+k2=k$$

[0013] Among these compounds, since the compound which does not have CH association is excellent in stability, it is still more desirable. Although the values of k are 1-100, since mixing with a perfluoro sulfonic-acid polymer will become difficult or it will be hard coming to dissolve it if too large, 50 or less are desirable, and 30 or less are still more desirable. Moreover, in the case of the compound which has especially a carboxylic-acid radical and a sulfonic group by the addition effectiveness becoming small if the value of k is too small, since it becomes easy to melt into water, two or more are desirable, and three or more are still more desirable. Moreover, it can also be made to fix by carrying out a polymerization, after forming a catalyst bed in the case of the compound which has a trifluoro vinyl group in intramolecular.

[0014] Although the effectiveness which raises oxygen permeability is acquired by making such a fluorine-containing ether compound contain, such a fluorine-containing ether compound also has the effectiveness which discharges promptly the water generated from having moderate water repellence, and is presumed to have contributed to the improvement in the engine performance when considering as a fuel cell too. In electrode catalyst coating of this invention, the content of the fluorine-containing ether compound expressed with a general formula (2) is used in 5 - 70% of the weight of the range. It is 20 - 50 % of the weight still more preferably ten to 60% of the weight preferably. If the addition effectiveness is scarce when there is less content than 5 % of the weight, and 70 % of the weight is exceeded, it will be hard coming to maintain the catalyst bed which became soft too much and was stabilized.
[0015] The method of infiltrating the solution of this constituent etc. is in the catalyst bed of the approach of usually mixing the solution of this constituent with the binder added catalyst powder and if needed using this constituent as an approach of using as electrode catalyst coating of the catalyst bed of a gas diffusion electrode, fabricating this, and forming a catalyst bed, and the gas diffusion electrode formed beforehand, and the any may be adopted as it. Therefore, generally this constituent will be used as a solution. Moreover, the solution of the fluorine-containing ether of a general formula (2) may be infiltrated into the catalyst bed formed using the conventional gas diffusion electrode, i.e., the perfluoro sulfonic-acid polymer of a general formula (1), as electrode catalyst coating, and a constituent may be made to form in it.
[0016] As a solvent in the case of using this constituent as a solution, the mixed solvent of fluorine-containing alcohols, such as lower alcohol, such as a methanol, ethanol, 1-propanol, 2-propanol, and a butanol, 2 and 2, 2-trifluoro ethanol, 2, 2, 3 and 3, 3-pentafluoro propanol, hexafluoro isopropanol, 2, 2 and 3, and 3-tetrafluoro propanol, and those alcohol is used. In addition, fluorine-containing compounds, such as hydro fluorocarbon and the hydro fluoro ether, an ether compound, ketones, amides, a nitryl compound, dimethyl sulfoxide, etc. may be used as independent or a mixed solvent, and the mixed solvent of these independent or mixed solvents, and water may be used further. 3 - 20% of the weight of a thing is usually used that the concentration of this constituent solution should just be the suitable concentration for formation of a catalyst bed.
[0017] The property is demonstrated when electrode catalyst coating of this invention is used for a cathode side, since oxygen gas permeability was high. Therefore, although using for a cathode side is indispensable, even if it uses also for an anode side, it does not interfere. In addition, since electrode catalyst coating like this invention is called an electrode catalyst binder or a jointing material for corrugated fibreboard from the point of the function and there is no clear distinction in the function corresponding to each name, similarly it is contained in this invention. that is, although electrode catalyst coating may exist in a part of catalyst bed, it is desirable for a catalyst bed to boil all, to exist and to also have a function as a binder. Moreover, if this coating is prepared where ion exchange membrane is touched when ion exchange membrane and a gas diffusion electrode are joined, it can act as a jointing material for corrugated fibreboard, and can heighten the junction force of ion exchange membrane and a gas diffusion electrode.
[0018] Next, the film / electrode zygote using electrode catalyst coating of this invention are explained. If the configuration is explained, as ion exchange membrane, "Nafion" which is the homogeneous membrane of a perfluoro sulfonic-acid polymer, and "ASHIPU REXX-S" by Asahi Chemical Industry Co., Ltd. can be used first. As thickness of ion exchange membrane, a 10-300-micrometer thing is used, for example. If ion exchange membrane is thinner than 10 micrometers, reinforcement at the time of membrane formation cannot be maintained, but if thicker than 300 micrometers, resistance of ion exchange membrane will increase and the output characteristics at the time of fuel cell actuation will decline. The thickness of desirable ion exchange membrane is about 30-150 micrometers. If there is need in the film, the core material for reinforcement can be prepared. Moreover, what doped the above-mentioned perfluoro sulfonic-acid polymer can also be used for porous film, such as polytetrafluoroethylene.
[0019] The gas diffusion electrode used for the film / electrode zygote is constituted by the electric conduction material which supported the particle of a catalyst metal, and the layer which consists of water repellent contained if needed [that water repellent and a binder may be contained if needed / the electric conduction material and if needed] are not supporting the catalyst again, or a binder may

be formed in the outside of a catalyst bed. If it is the metal which promotes oxidation reaction of hydrogen, and the reduction reaction of oxygen as a catalyst metal used for this gas diffusion electrode, which thing may be used, for example, platinum, gold, silver, palladium, iridium, a rhodium, a ruthenium, iron, cobalt, nickel, chromium, a tungsten, manganese, vanadium, or those alloys will be mentioned. In such a catalyst, when especially platinum is many, it is used. The particle size of the metal used as a catalyst is usually 10-300A. The amount of support of a catalyst is 0.01 - 10 mg/cm2, where an electrode is fabricated. It carries out.

[0020] As electric conduction material, if it is the electronic conductive matter, which thing may be used, for example, various metals, a carbon material, etc. will be mentioned. as a carbon material, for example, carbon black, such as furnace black, channel black, and acetylene black, activated carbon, a graphite, etc. are mentioned, and these are independent -- or it is mixed and used. As water repellent, fluorination carbon etc. is used, for example. Although it is desirable to use catalyst coating of this invention as it is as a binder, it does not interfere, even if it uses other various resin. In that case, the fluorine-containing resin which has water repellence is desirable, and the outstanding thing especially heat-resistant and oxidation-resistant is more desirable, for example, a polytetrafluoroethylene and tetrafluoroethylene-perfluoroalkyl vinyl ether copolymer and a tetrafluoroethylene-hexafluoropropylene copolymer are mentioned.

[0021] Junction to ion exchange membrane and a gas diffusion electrode is carried out using the equipment which can be pressurized and warmed. Generally, it is performed by a hotpress machine, the roll press machine, etc. Generally the press temperature in that case is 120 degrees C - 250 degrees C that what is necessary is just more than the glass transition temperature of ion exchange membrane. although it depends for a press pressure on the hardness of the gas diffusion electrode to be used -- usually -- 5-200kg/cm2 it is . 5kg/cm2 Joining to ion exchange membrane and an electrode becomes inadequate [the following], and it is 200kg/cm2. If it exceeds, the hole of a gas diffusion electrode will be crushed. the range where a press pressure is desirable -- 20-100kg/cm2 it is .

[0022] The zygote of the ion exchange membrane and the gas diffusion electrode which were formed as mentioned above is inserted between the flanges made from graphite of two sheets which extracted with a charge collector and gas intake and were equipped with opening, and is assembled as a fuel cell. Here, it operates as a fuel cell by supplying the gas (oxygen or air) which contains oxygen in the gas diffusion electrode of another side for the hydrogen gas which is a fuel to one gas diffusion electrode. Since the direction which operates a fuel cell at high temperature does not function as the ion exchange membrane used as an electrolyte not having moisture although it is desirable in order that the catalytic activity of an electrode may go up and an electrode overvoltage may decrease, it needs to make it operate at the temperature in which moisture management is possible. The range where the operating temperature of a fuel cell is desirable is room temperature - 100 degree C. As shown above, electrode catalyst coating of this invention shows the engine performance which was excellent when it used for the gas diffusion electrode of a polymer electrolyte fuel cell. Although it is not necessarily clear whether it is that to which this improvement in the engine performance originates only in high oxygen gas permeability, also when air is used as an oxidizer, since high output voltage is conventionally obtained compared with an ingredient, it is desirable on industry.

[0023]

[Embodiment of the Invention] An example explains this invention to a detail further below.

[Example] <an example 1> (composition of a fluorine-containing ether compound (3)) -- the following acid full ora -- the id (PCR company make) -- 20ml water was dropped at mixture (12.5g and ether 50ml) (two-layer separation), stirring under ice-cooling. During dropping, it once became a homogeneity solution and two-layer separation was carried out again after that.

[Formula 6]

$$FOC-\underset{\displaystyle CF_3}{\underset{|}{C}}F-(OCF_2\underset{\displaystyle CF_3}{\underset{|}{C}}F)\,4\text{-}7-OCF_2CF_2CF_3$$

[0024] After dropping termination, after continuing stirring for 3 hours, liquids were separated and the ether extracted the aqueous phase 3 times. After it collected ether phases and saturation brine

washed twice, the ether was distilled off and 12.6g of colorless oily matter was obtained. It checked that they were NMR and the fluorine-containing ether compound which contains a following-type (3) carboxylic acid from an IR spectrum.
[Formula 7]

$$HOOC-\underset{CF_3}{CF}-(OCF_2\underset{CF_3}{CF})_n-OCF_2CF_2CF_3 \qquad (3) \qquad n \fallingdotseq 5$$

[0025] (Measurement of oxygen gas permeability) It added so that the weight ratio of a polymer and an ether compound might be set to 8:2, and the fluorine-containing ether compound of the above-mentioned formula (3) was used as the homogeneity solution at the solution which dissolved the perfluoro sulfonic-acid polymer (ASHIPU REXX - S, Asahi Chemical Industry Co., Ltd. make) with an exchange capacity of 950g [/Eq] in the mixed solvent (weight ratio 1:1) of n-propanol and 2, 2, 3, 3, and 3-pentafluoro propanol by 5% of the weight of concentration. This solution was developed on the petri dish, after being air-dry, the vacuum drying was carried out at 80 degrees C, and the film of 42 micrometers of thickness was produced. After this film was immersed in water, surface water was wiped off and oxygen gas permeability was measured using the flow type gas permeability gaging system (the product made from YANACO, GTR-100FA). Consequently, the oxygen gas transmission coefficients when making test gas into humidification air and making cel temperature into 40 degrees C were 5.0x10-9 cc, cm/cm2, sec, and cmHg. The measured value in the film of only the perfluoro sulfonic-acid polymer produced without adding the above-mentioned fluorine-containing ether compound for a comparison was 2.5x10-9cc, cm/cm2, sec, and cmHg.
[0026] (Production of the film / electrode zygote) To 40% of the weight of platinum catalyst support carbon (product made from U.S. E-TEK), the above-mentioned solution was added so that the weight ratio of a platinum catalyst and a polymer + fluorine-containing ether compound might be set to 2:1, homogeneity was distributed to it, and the paste was prepared to it. After applying this paste on a Teflon sheet using the screen of 200 meshes so that it may be set to catalyst area 2cmx2cm, it dries and fixes at 100 degrees C among an atmospheric-air ambient atmosphere, and it is amount of platinum support 0.25 mg/cm2. The catalyst sheet was obtained. 100 micrometers in the exchange capacity of 950g/Eq and thickness and the film surface product 3cmx3cm perfluoro sulfonic-acid polymer film (ASHIPU REXX - S1004, Asahi Chemical Industry Co., Ltd. make) are inserted for the catalyst bed of the catalyst sheet of two sheets facing each other and between them, and they are 150 degrees C and the pressure of 50kg/cm2. After carrying out a hotpress, the double-sided Teflon sheet was removed and the film / electrode zygote was produced.
[0027] After being immersed in Teflon dispersion liquid (60 % of the weight), using a carbon cross (product made from E-TEK) with a thickness of about 400 micrometers as a catalyst bed base material, sintering was performed at 340 degrees C and it was made to sink in 40% of the weight to a carbon cross. The voidage was 50%. The laminating of these film / electrode zygote, and the catalyst bed base material was carried out, and it included in fuel cell single cel evaluation equipment, and hydrogen gas was used for the fuel, air was used for the oxidizer, and the single cel characteristic test was performed at ordinary pressure and the cel temperature of 80 degrees C. Hydrogen gas humidified at 90 degrees C, and air was not humidified but was supplied to the cel as it was. Consequently, 0.5 and 1.0 A/cm2 The cel output voltage at the time of current density was 0.65V and 0.50V, respectively.
[0028] <Example 2> In the mixed solution of a perfluoro sulfonic-acid polymer and the fluorine-containing ether compound of the above-mentioned formula (3), when the film was produced like the example 1 and oxygen gas permeability was measured except having set the weight ratio of a polymer and an ether compound to 6:4, oxygen gas transmission coefficients were 6.5x10-9 cc, cm/cm2, sec, and cmHg. Moreover, when the film / electrode zygote was produced using the solution of this constituent and the single cel characteristic test was performed, they are 0.5 and 1.0 A/cm2. The cel output voltage at the time of current density was 0.66V and 0.57V, respectively.
[0029] <Example 3> (composition of a fluorine-containing ether compound (5)) After mixing tetrafluoroethylene with a sulfuric anhydride (SO3) in a proof-pressure container, the product was distilled (42 degrees C of boiling points), and the 2-hydroxy tetrapod FUROORO ethane-sulfonic-acid sultone was obtained. Where this 2-hydroxy tetrafluoro ethane-sulfonic-acid sultone is ice-

cooled, ring breakage of the little triethylamine was added and carried out, and fluoro sulfonyl difluoro ASECHIRUFURUORAIDO (FOCCF2 SO2 F) was compounded. Next, fluoro sulfonyl difluoro ASECHIRUFURUORAIDO 50g and 6.0g of desiccation cesium fluorides and desiccation jig lime 50ml were put into the proof-pressure container, and hexafluoropropylene oxide about 380g was pressed fit in several steps under ice-cooling. It was made to react at 0 degree C then for 8 hours, and 32g of components of the boiling point - 100 degrees C / 3mmHg was obtained. It checked that it was a following-type (4) compound from NMR of the methyl ester which a part of product was made to react with a methanol, and was obtained, and an IR spectrum.

[Formula 8]

$$FOC-\underset{\displaystyle CF_3}{\underset{|}{C}}F-(OCF_2\underset{\displaystyle CF_3}{\underset{|}{C}}F)n-OCF_2CF_2SO_2F \qquad (4) \qquad n \fallingdotseq 4$$

[0030] The above-mentioned compound (4) To 5.0g, 5g of NaOH water solutions was added 40%, and it stirred at 100 degrees C for 5 hours, and stirred at 190 degrees C succeedingly for 5 hours. It was made acidity with the sulfuric acid 35% after cooling to the room temperature, and the ether extracted. The ether phase was condensed and 3.2g of oily matter of light brown was obtained. It checked that it was a following-type (5) fluorine-containing ether compound from NMR and an IR spectrum. The value of n was again checked by NMR.

[Formula 9]

$$CF_3CHF-(OCF_2\underset{\displaystyle CF_3}{\underset{|}{C}}F)n-OCF_2CF_2SO_3H \qquad (5) \qquad n \fallingdotseq 4$$

[0031] (Measurement of oxygen gas permeability, and production of the film / electrode zygote) When the film was produced like the example 1 and oxygen gas permeability was measured except having used the compound of the above-mentioned formula (5) as a fluorine-containing ether compound, oxygen gas transmission coefficients were 5.7x10-9cc, cm/cm2, sec, and cmHg. Moreover, when the film / electrode zygote was produced using the solution of this constituent and the single cel characteristic test was performed, they are 0.5 and 1.0 A/cm2. The cel output voltage at the time of current density was 0.68V and 0.54V, respectively.

[0032] <Example 4> In the mixed solution of a perfluoro sulfonic-acid polymer and the fluorine-containing ether compound of the above-mentioned formula (5), when the film was produced like the example 3 and oxygen gas permeability was measured except having set the weight ratio of a polymer and an ether compound to 6:4, oxygen gas transmission coefficients were 1.9x10-8cc, cm/cm2, sec, and cmHg. Moreover, when the film / electrode zygote was produced using the solution of this constituent and the single cel characteristic test was performed, they are 0.5 and 1.0 A/cm2. The cel output voltage at the time of current density was 0.69V and 0.58V, respectively.

[0033] <Example 5> (composition of a fluorine-containing ether compound (6)) 5.0g of compounds of the above-mentioned formula (4) compounded in the example 3 was melted to the 10ml perfluoro hexane, and after adding 5g of NaOH water solutions 40% and stirring at a room temperature for 1 hour, it stirred at reflux temperature (65 degrees C) for 5 hours. The white solid-state which filtered after cooling and was obtained to the room temperature was melted to ethanol, insoluble matter was filtered and removed, filtrate was condensed, and white powder was obtained. The obtained powder was made into acidity with the sulfuric acid 35%, the ether extracted, the ether phase was condensed, and 2.9g of oily matter of light brown was obtained. It checked that it was a following-type (6) fluorine-containing ether compound from NMR and an IR spectrum.

[Formula 10]

$$HOOC-\underset{\displaystyle CF_3}{\underset{|}{C}}F-(OCF_2\underset{\displaystyle CF_3}{\underset{|}{C}}F)n-OCF_2CF_2SO_3H \qquad (6) \qquad n \fallingdotseq 4$$

[0034] (Measurement of oxygen gas permeability, and production of the film / electrode zygote) When the film was produced like the example 1 and oxygen gas permeability was measured except having used the compound of the above-mentioned formula (6) as a fluorine-containing ether compound, oxygen gas transmission coefficients were 5.8x10-9cc, cm/cm2, sec, and cmHg.

Moreover, when the film / electrode zygote was produced using the solution of this constituent and the single cel characteristic test was performed, they are 0.5 and 1.0 A/cm2. The cel output voltage at the time of current density was 0.68V and 0.55V, respectively.
[0035] <Example 6> In the mixed solution of a perfluoro sulfonic-acid polymer and the fluorine-containing ether compound of the above-mentioned formula (6), when the film was produced like the example 5 and oxygen gas permeability was measured except having set the weight ratio of a polymer and an ether compound to 6:4, oxygen gas transmission coefficients were 2.7x10-8cc, cm/cm2, sec, and cmHg. Moreover, when the film / electrode zygote was produced using the solution of this constituent and the single cel characteristic test was performed, they are 0.5 and 1.0 A/cm2. The cel output voltage at the time of current density was 0.70V and 0.59V, respectively.
[0036] <Example 7> (composition of a fluorine-containing ether compound (7)) After 10g of compounds of the above-mentioned formula (4) compounded in the example 3 was dropped at 10g of potassium carbonate which carried out the vacuum drying at 180 degrees C to just before, they were heated at 130 degrees C for 2 hours, and were heated at 190 more degrees C for 2 hours. Water was added after cooling to the room temperature, the ether extracted further, and the obtained oily matter was melted to the 20ml perfluoro hexane after distilling off the ether, and after adding 10g of NaOH water solutions 40% and stirring at a room temperature for 1 hour, it stirred at reflux temperature (65 degrees C) for 5 hours. The white solid-state which filtered after cooling and was obtained to the room temperature was melted to ethanol, insoluble matter was filtered and removed, filtrate was condensed, and white powder was obtained. The obtained powder was made into acidity with the sulfuric acid 35%, the ether extracted, the ether phase was condensed, and 4.5g of oily matter of light brown was obtained. It checked that it was a following-type (7) fluorine-containing ether compound from NMR and an IR spectrum.
[Formula 11]

$$CF_2{=}CF-(OCF_2\underset{\displaystyle CF_3}{\underset{|}{C}}F)_n-OCF_2CF_2SO_3H \qquad (7) \qquad n \fallingdotseq 4$$

[0037] (Measurement of oxygen gas permeability, and production of the film / electrode zygote) When the film was produced like the example 2 and oxygen gas permeability was measured except having used the compound of the above-mentioned formula (7) as a fluorine-containing ether compound, oxygen gas transmission coefficients were 1.2x10-8cc, cm/cm2, sec, and cmHg. Moreover, when the film / electrode zygote was produced using the solution of this constituent and the single cel characteristic test was performed, they are 0.5 and 1.0 A/cm2. The cel output voltage at the time of current density was 0.68V and 0.57V, respectively.
[0038] <Example 8> (composition of a fluorine-containing ether compound (8)) 2.0g of compounds of the above-mentioned formula (7) compounded in the example 7 is melted to the 10ml carbon tetrachloride, and chlorine gas was blown at the room temperature. After the reaction, the solvent was distilled off and 2.2g of oily matter of light brown was obtained. It checked that it was a following-type (8) fluorine-containing ether compound from NMR and an IR spectrum.
[Formula 12]

$$CClF_2CClF-(OCF_2\underset{\displaystyle CF_3}{\underset{|}{C}}F)_n-OCF_2CF_2SO_3H \qquad (8) \qquad n \fallingdotseq 4$$

[0039] (Measurement of oxygen gas permeability, and production of the film / electrode zygote) When the film was produced like the example 2 and oxygen gas permeability was measured except having used the compound of the above-mentioned formula (8) as a fluorine-containing ether compound, oxygen gas transmission coefficients were 1.7x10-8cc, cm/cm2, sec, and cmHg. Moreover, when the film / electrode zygote was produced using the solution of this constituent and the single cel characteristic test was performed, they are 0.5 and 1.0 A/cm2. The cel output voltage at the time of current density was 0.69V and 0.58V, respectively.
[0040] <Example 1 of a comparison> Except not adding a fluorine-containing ether compound, the film / electrode zygote was produced like the example 1, and the single cel characteristic test was performed. Consequently, 0.5 and 1.0 A/cm2 The cel output voltage at the time of current density

was 0.60V and 0.44V, respectively.
[0041]
[Effect of the Invention] When electrode catalyst coating of this invention is used for the gas diffusion electrode of a polymer electrolyte fuel cell and air is used as an oxidizer, compared with an ingredient, high output voltage is obtained conventionally. Therefore, the film / electrode zygote using electrode catalyst coating of this invention are also excellent compared with the conventional thing.

[Translation done.]

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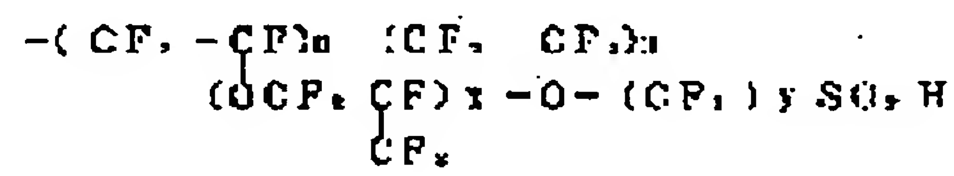
(54) ELECTRODE CATALYST COATING AGENT FOR FUEL CELL AND MEMBRANE/ELECTRODE JOINT BODY USING SAME COATING AGENT

(57)Abstract:
PROBLEM TO BE SOLVED: To lower an oxygen-concentration overvoltage when normal-pressure air is supplied and provide a high output voltage, by using a composition comprising a perfluorosulfonic-acid polymer and a fluorine-containing ether compound as an electrode-catalyst coating agent used for a gas diffusion electrode.
SOLUTION: A membrane/electrode joint body for a solid high-polymer type fuel cell comprises an ion-exchange membrane serving as an electrolyte and a gas diffusion electrode jointed to the ion-exchange membrane. An electrode- catalyst coating agent used for the gas diffusion electrode contains a perfluorosulfonic-acid polymer of 30 to 95 wt.% expressed by an expression I and a fluorine-containing ether compound of 5 to 70 wt.% expressed by an expression II. In the expression I, x=0 to 2, y=2 to 3, and n/m=1 to 10. In the expression II, Rf is a perfluoroalkylene group having the C number of 1 to 3, x and y are perfluoroalkyl groups having the C number of 1 to 5, and k is 1 to 100. The gas diffusion electrode using the electrode-catalyst coating agent is used at least on the side of a cathode.



I

$$X-(ORf)_k-O-Y$$

II

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(54)【発明の名称】　燃料電池用電極触媒被覆剤及び該被覆剤を用いた膜／電極接合体

(57)【要約】

【課題】　新規の電極触媒被覆剤及び該電極触媒被覆剤を用いることで常圧の空気を供給しても、高い出力電圧が得られる固体高分子型燃料電池用膜／電極接合体を提供する。

【解決手段】　パーフルオロスルホン酸ポリマーを30～95重量%、下記一般式（1）で表される含フッ素エーテル化合物を5～70重量%の範囲で含有する組成物からなる電極触媒被覆剤及び該電極触媒被覆剤を用いた膜／電極接合体。

【化1】

X－（ORf）k －O－Y　　（1）

（ここで、Rfは単一または複数の種類の、炭素数1～3個のパーフルオロアルキレン基、X、Yは炭素数1～5個のパーフルオロアルキル基で、2重結合を含んでいてもよく、各炭素にはH、Cl、Br、SO_3H、COOR基から選ばれる基が各炭素につき1個まで置換していてもよい。RはHまたはアルキル基である。また、k＝1～100の範囲である。）

【特許請求の範囲】

【請求項1】 電解質となるイオン交換膜と、このイオン交換膜に接合されるガス拡散電極とで構成される固体高分子型燃料電池用膜／電極接合体において、該ガス拡散電極に用いられる電極触媒被覆剤であって、一般式（1）で表されるパーフルオロスルホン酸ポリマーを30～95重量%、一般式（2）で表される含フッ素エーテル化合物を5～70重量%の範囲で含有する組成物からなる電極触媒被覆剤。

【化1】

$$-(CF_2-\underset{\displaystyle (OCF_2\underset{\displaystyle CF_3}{\underset{|}{C}}F)_x-O-(CF_2)_ySO_3H}{\underset{|}{C}}F)_m-(CF_2-CF_2)_n- \qquad (1)$$

（ここで、$x=0$～2の整数、$y=2$～3の整数、$n/m=1$～10である。）

【化2】

$$X-(ORf)_k-O-Y \qquad (2)$$

（ここで、Rfは単一または複数の種類の、炭素数1～3個のパーフルオロアルキレン基、X、Yは炭素数1～5個のパーフルオロアルキル基で、2重結合を含んでいてもよく、各炭素にはH、Cl、Br、SO_3H、COOR基から選ばれる基が各炭素につき1個まで置換していてもよい。RはHまたはアルキル基である。また、$k=1$～100の範囲である。）

【請求項2】 請求項1記載の電極触媒被覆剤を用いたガス拡散電極を少なくともカソード側に用いたことを特徴とする固体高分子型燃料電池用膜／電極接合体。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は固体高分子型燃料電池を構成するガス拡散電極に用られる電極触媒被覆剤に関し、該電極触媒被覆剤を用いたガス拡散電極を有する、固体高分子型燃料電池用膜／電極接合体に関するものである。

【0002】

【従来の技術】燃料電池は、電池内で水素やメタノール等の燃料を電気化学的に酸化することにより、燃料の化学エネルギーを直接電気エネルギーに変換して取り出すものであり、近年、クリーンな電気エネルギー供給源として注目されている。特にイオン交換膜を電解質として用いる固体高分子型燃料電池は、高出力密度が得られ、低温作動が可能なことから電気自動車用電源として期待されている。

【0003】このような固体高分子型燃料電池の基本構造は、固体電解質であるイオン交換膜と、その両面に接合された一対のガス拡散電極とで構成され、各ガス拡散電極の少なくともイオン交換膜側には触媒が担持されている。そして、一方のガス拡散電極に燃料である水素を、もう一方のガス拡散電極に酸化剤である酸素または空気をそれぞれ供給し、両方のガス拡散電極間に外部負荷回路を接続することにより、燃料電池として作動する。即ち、前者のガス拡散電極（アノード）においては、燃料の酸化によりプロトンと電子とが生じ、このプロトンは電解質内を伝導して後者のガス拡散電極（カソード）に移動し、ここでプロトンと酸化剤中の酸素とが反応して水を生成する。この時、アノードで生じた電子が、外部負荷回路を移動してカソードへと移動することにより電気エネルギーが得られる。

【0004】このような固体高分子型燃料電池においては、ガス拡散電極に担持されている触媒上へのプロトン移動を媒介し、該触媒の利用効率を高める目的で、プロトン伝導性高分子電解質が電極触媒被覆剤として用いられている。現在、固体高分子型燃料電池に主として使用されているプロトン伝導性高分子電解質は、米国デュポン社製の「ナフィオン（登録商標）」や旭化成工業（株）製の「アシプレックス－S（登録商標）」等に代表されるパーフルオロスルホン酸含有ポリマーである。これらのポリマーは強酸性基を有し、高い化学的安定性を有することから電解質としてのイオン交換膜として使用されている他、その溶液はガス拡散電極の触媒層の電極触媒被覆剤として使用することが提案されている（例えば特公平2－7398号公報、特開平3－208260号公報等）。

【0005】しかしながら、従来用いられている電極触媒被覆剤では触媒層への該被覆剤を通しての酸素供給能力が不充分なために、酸素濃度過電圧が高いという欠点を有していた。従って高い出力電圧を得ようとすれば、酸素を加圧したり濃度を高めて供給するなどの手段が必要であり、そのためには電池全体として高価なシステムが必要であった。このことから、空気を常圧で供給しても高い出力電圧が得られるような、酸素濃度過電圧の低い電極触媒被覆剤が望まれていた。

【0006】

【発明が解決しようとする課題】本発明者らは、従来用いられているパーフルオロスルホン酸ポリマーとある種の含フッ素エーテル化合物とからなる組成物が高い酸素透過性を有することから、これを電極触媒被覆剤として用いることで常圧の空気を供給したときの酸素濃度過電圧を低下させることができ、高い出力電圧が得られる固体高分子型燃料電池用膜／電極接合体が得られることを見いだし、本発明に至った。

【0007】

【発明を解決するための手段】すなわち本発明は下記の

通りである。

１．電解質となるイオン交換膜と、このイオン交換膜に接合されるガス拡散電極とで構成される固体高分子型燃料電池用膜／電極接合体において、該ガス拡散電極に用いられる電極触媒被覆剤であって、一般式（１）で表されるパーフルオロスルホン酸ポリマーを３０～９５重量＊％、一般式（２）で表される含フッ素エーテル化合物を５～７０重量％の範囲で含有する組成物からなる電極触媒被覆剤。

【０００８】

【化３】

$$-(CF_2-\underset{\substack{| \\ (OCF_2\underset{\substack{| \\ CF_3}}{C}F)_x-O-(CF_2)_y SO_3H}}{C}F)_m-(CF_2-CF_2)_n- \qquad (1)$$

（ここで、ｘ＝０～２の整数、ｙ＝２～３の整数、ｎ／ｍ＝１～１０である。）

【０００９】

【化４】

$$X-(ORf)_k-O-Y \qquad (2)$$

（ここで、Ｒｆは単一または複数の種類の、炭素数１～３個のパーフルオロアルキレン基、Ｘ、Ｙは炭素数１～５個のパーフルオロアルキル基で、２重結合を含んでいてもよく、各炭素にはＨ、Ｃｌ、Ｂｒ、SO_3H、ＣＯＯＲ基から選ばれる基が各炭素につき１個まで置換していてもよい。ＲはＨまたはアルキル基である。また、ｋ＝１～１００の範囲である。）

２．上記１の電極触媒被覆剤を用いたガス拡散電極を少なくともカソード側に用いたことを特徴とする固体高分子型燃料電池用膜／電極接合体。

【００１０】以下本発明の電極触媒被覆剤の構成要素について、順次説明する。まず一般式（１）で表される構造を有するパーフルオロスルホン酸ポリマーについて、まずｘ＝０～２の範囲のものを用いることができるが、製造や重合が容易なのでｘ＝１が好ましい。また、ｎ／ｍ＝１～１０の範囲で用いることが可能だが、高分子量体が得られやすく、溶媒にも溶解しやすいのでｎ／ｍ＝２～７が好ましい。従って、デュポン社製の「ナフィオン」や旭化成工業（株）製の「アシプレックス－Ｓ」等、従来から用いられているパーフルオロスルホン酸ポリマーをそのまま用いることができる。

【００１１】次に、一般式（２）で表される含フッ素エーテル化合物について説明する。一般式（２）においてＲｆは単一または複数の種類の、炭素数１～３個のパーフルオロアルキレン基である。具体的には$-CF_2-$、$-CF_2CF_2-$、$-CF_2CF_2CF_2-$、$-CF_2CF(CF_3)-$等であり、分子内に２種以上を混合して有していてもよい。これらの中では$-CF_2CF(CF_3)-$を含むものが特に好ましい。また、Ｘ、Ｙは炭素数１～５個のパーフルオロアルキル基で、炭素数１～３個のものが好ましく、２重結合を含んでいてもよい。各炭素にはＨ、Ｃｌ、Ｂｒ、SO_3H、ＣＯＯＲ基から選ばれる基が各炭素につきそれぞれ１個まで置換していてもよい。ＲはＨまたはアルキル基であり、アルキル基の場合、炭素数１～３個のものが好ましい。Ｘ、Ｙは同一でも異なっていてもよい。具体例を例示すれば、CF_3-、CF_3CF_2-、$CF_3CF_2CF_2-$、CF_3CHF-、$CF_2=CF-$、CHF_2CHF-、$CClF_2CClF-$、$CBrF_2CBrF-$、$HOOCCF_2-$、CH_3OOCCF_2-、$HOOCCF(CF_3)-$、$CH_3OOCCF(CF_3)-$、$HO_3SCF_2CF_2-$、$HO_3SCF_2CF_2CF_2-$、$HO_3S-CF(CF_3)CF_2-$等の基が挙げられる。これらの組み合わせからなる化合物のうち、溶液化しやすく、パーフルオロスルホン酸ポリマーとも混合しやすいので少なくとも分子内に１～２個のＣＯＯＨ基または／およびSO_3H基を有する化合物が好ましい。具体的には以下のような化合物を例示することができる。

【００１２】

【化５】

$$HOOC-CF(CF_3)-(OCF_2CF(CF_3))_k-OCF_2CF_2CF_3$$

$$HOOC-CF(CF_3)-(OCF_2CF(CF_3))_k-OCF_2CF_2SO_3H$$

$$HOOC-CF(CF_3)-(OCF_2CF(CF_3))_k-OCF_2CF_2CF_2SO_3H$$

$$HOOC-CF(CF_3)-(OCF_2CF(CF_3))_k-OCF_2CF_2COOH$$

$$HOOC-CF(CF_3)-(OCF_2CF(CF_3))_k-OCF_2CF(CF_3)SO_3H$$

$$CF_2=CF-(OCF_2CF(CF_3))_k-OCF_2CF_2SO_3H$$

$$CF_2=CF-(OCF_2CF(CF_3))_k-OCF_2CF_2CF_2SO_3H$$

$$CF_2=CF-(OCF_2CF(CF_3))_k-OCF_2CF_2COOH$$

$$CClF_2CClF-(OCF_2CF(CF_3))_k-OCF_2CF_2SO_3H$$

$$CClF_2CClF-(OCF_2CF(CF_3))_k-OCF_2CF_2COOH$$

$$CHF_2CHF-(OCF_2CF(CF_3))_k-OCF_2CF_2SO_3H$$

$$CHF_2CHF-(OCF_2CF(CF_3))_k-OCF_2CF_2COOH$$

$$CF_3CHF-(OCF_2CF(CF_3))_k-OCF_2CF_2SO_3H$$

$$CF_3CHF-(OCF_2CF(CF_3))_k-OCF_2CF_2COOH$$

$$HOOCCF_2-(OCF_2CF(CF_3))_{k1}-(OCF_2)_{k2}-OCF_2COOH \quad k1+k2=k$$

$$HOOCCF_2-(OCF_2CF_2)_{k1}-(OCF_2)_{k2}-OCF_2COOH \quad k1+k2=k$$

【0013】これらの化合物中、ＣＨ結合を有さない化合物が安定性に優れるのでさらに好ましい。ｋの値は１〜１００であるが、大きすぎるとパーフルオロスルホン酸ポリマーとの混合が困難になったり、相溶しにくくなったりするので５０以下が好ましく、３０以下がさらに好ましい。またｋの値が小さすぎると添加効果が小さくなり、特にカルボン酸基やスルホン酸基を有する化合物の場合は水に溶けやすくなったりするので２以上が好ましく、３以上がさらに好ましい。また、分子内にトリフルオロビニル基を有する化合物の場合は、触媒層を形成後に重合させることで固定化させることもできる。

【００１４】このような含フッ素エーテル化合物を含有させることで、酸素透過性を高める効果が得られるが、その他にもこのような含フッ素エーテル化合物は適度の撥水性も有することから生成した水を速やかに排出する効果も有し、やはり燃料電池としたときの性能向上に寄与していると推定される。本発明の電極触媒被覆剤においては、一般式（２）で表される含フッ素エーテル化合物の含有率は５〜７０重量%の範囲で用いられる。好ましくは１０〜６０重量%、さらに好ましくは２０〜５０重量%である。含有率が５重量%より少ないと添加効果が乏しく、７０重量%を越えると柔らかくなりすぎて安

定した触媒層を維持しにくくなる。

【0015】該組成物を用いて、ガス拡散電極の触媒層の電極触媒被覆剤として用いる方法としては、通常、該組成物の溶液を、触媒粉末および必要に応じて添加される結着剤等と混合し、これを成形して触媒層を形成する方法、予め形成されたガス拡散電極の触媒層に、該組成物の溶液を含浸させる方法等があり、そのいずれを採用してもよい。従って、一般に該組成物は溶液として用いられることになる。また、従来のガス拡散電極、即ち一般式（１）のパーフルオロスルホン酸ポリマーのみを電極触媒被覆剤として用いて形成した触媒層に、一般式（２）の含フッ素エーテルの溶液を含浸させ、組成物を形成させてもよい。

【0016】該組成物を溶液として用いる場合の溶媒としては、メタノール、エタノール、１－プロパノール、２－プロパノール、ブタノール等の低級アルコール類、２，２，２－トリフルオロエタノール、２，２，３，３，３－ペンタフルオロプロパノール、ヘキサフルオロイソプロパノール、２，２，３，３－テトラフルオロプロパノール等の含フッ素アルコール類、それらのアルコールの混合溶媒が用いられる。その他ハイドロフルオロカーボンやハイドロフルオロエーテル等の含フッ素化合物、エーテル化合物、ケトン類、アミド類、ニトリル化合物、ジメチルスルホキシド等を単独あるいは混合溶媒として用いてもよく、さらにはこれらの単独または混合溶媒と水との混合溶媒を用いてもよい。該組成物溶液の濃度は、触媒層の形成に適当な濃度であればよく、通常３～２０重量%のものが用いられる。

【0017】本発明の電極触媒被覆剤は酸素ガス透過性が高いことからカソード側に用いたときにその特性が発揮される。従ってカソード側に用いることが必須であるが、アノード側にも用いても差し支えない。尚、本発明のような電極触媒被覆剤は、その機能の点から電極触媒バインダーまたは接合材と称されることもあり、それぞれの呼称に対応する機能には明確な区別はないので、同じく本発明に含まれるものである。即ち、電極触媒被覆剤は、触媒層の一部にのみ存在していてもよいが、触媒層の全部に存在してバインダーとしての機能も有することが好ましい。また、この被覆剤は、イオン交換膜とガス拡散電極とを接合した時に、イオン交換膜に接した状態で設けられていると、接合材として作用し、イオン交換膜とガス拡散電極との接合力を高めることができる。

【0018】次に、本発明の電極触媒被覆剤を用いた膜／電極接合体について説明する。その構成を説明すると、まずイオン交換膜としては、パーフルオロスルホン酸ポリマーの均一膜である「ナフィオン」や旭化成工業（株）製の「アシプレックス－Ｓ」を用いることができる。イオン交換膜の厚さとしては、例えば１０～３００μｍのものが用いられる。イオン交換膜が、１０μｍより薄いと成膜時の強度が保てず、３００μｍより厚いとイオン交換膜の抵抗が増大し燃料電池作動時の出力特性が低下する。好ましいイオン交換膜の厚さは３０～１５０μｍ程度である。膜には必要があれば、補強のための芯材を設けることができる。またポリテトラフルオロエチレン等の多孔膜に上記パーフルオロスルホン酸ポリマーをドープしたものを用いることもできる。

【0019】膜／電極接合体に使用されるガス拡散電極は、触媒金属の微粒子を担持した導電材により構成されるものであり、必要に応じて撥水剤や結着剤が含まれていてもよいまた、触媒を担持していない導電材と必要に応じて含まれる撥水剤や結着剤とからなる層が、触媒層の外側に形成してあるものでもよい。このガス拡散電極に使用される触媒金属としては、水素の酸化反応および酸素の還元反応を促進する金属であればいずれのものでもよく、例えば、白金、金、銀、パラジウム、イリジウム、ロジウム、ルテニウム、鉄、コバルト、ニッケル、クロム、タングステン、マンガン、バナジウム、あるいはそれらの合金が挙げられる。このような触媒の中で、特に白金が多くの場合用いられる。触媒となる金属の粒径は、通常は１０～３００オングストロームである。触媒の担持量は、電極が成形された状態で例えば０．０１～１０ｍｇ／ｃｍ^2 とする。

【0020】導電材としては、電子導伝性物質であればいずれのものでも良く、例えば各種金属や炭素材料などが挙げられる。炭素材料としては、例えば、ファーネスブラック、チャンネルブラック、およびアセチレンブラック等のカーボンブラック、活性炭、黒鉛等が挙げられ、これらが単独あるいは混合して使用される。撥水剤としては、例えばフッ素化カーボン等が使用される。バインダーとしては本発明の触媒被覆剤をそのまま用いることが好ましいが、他の各種樹脂を用いても差し支えない。その場合は撥水性を有する含フッ素樹脂が好ましく、特に耐熱性、耐酸化性の優れたものがより好ましく、例えばポリテトラフルオロエチレン、テトラフルオロエチレン－パーフルオロアルキルビニルエーテル共重合体、およびテトラフルオロエチレン－ヘキサフルオロプロピレン共重合体が挙げられる。

【0021】イオン交換膜とガス拡散電極との接合は、加圧、加温できる装置を用いて実施される。一般的には、例えば、ホットプレス機、ロールプレス機等により行われる。その際のプレス温度は、イオン交換膜のガラス転移温度以上であれば良く、一般的には１２０℃～２５０℃である。プレス圧力は、使用するガス拡散電極の固さに依存するが、通常、５～２００ｋｇ／ｃｍ^2 である。５ｋｇ／ｃｍ^2 未満では、イオン交換膜と電極との接合が不十分となり、２００ｋｇ／ｃｍ^2 を超えるとガス拡散電極の空孔がつぶされてしまう。プレス圧力の好ましい範囲は、２０～１００ｋｇ／ｃｍ^2 である。

【0022】以上のように形成されたイオン交換膜とガス拡散電極との接合体は、集電体とガス取り入れ口と抜

き出し口とを備えた二枚のグラファイト製フランジの間に挿入され、燃料電池として組み立てられる。ここで、一方のガス拡散電極には燃料である水素ガスを、他方のガス拡散電極には酸素を含むガス（酸素あるいは空気）を供給することにより燃料電池として作動する。燃料電池は、高い温度で作動させる方が、電極の触媒活性が上がり電極過電圧が減少するため望ましいが、電解質となるイオン交換膜は水分がないと機能しないため、水分管理が可能な温度で作動させる必要がある。燃料電池の作動温度の好ましい範囲は室温～１００℃である。以上示したように、本発明の電極触媒被覆剤は固体高分子型燃料電池のガス拡散電極に用いたときに優れた性能を示す。この性能向上が高い酸素ガス透過性だけに由来する＊ものかどうかは必ずしも明らかではないが、酸化剤として空気を用いたときにも、従来材料に比べて高い出力電圧が得られることから産業上好ましい。

【００２３】

【発明の実施の形態】以下実施例によって本発明をさらに詳細に説明する。

【実施例】〈実施例１〉

（含フッ素エーテル化合物（３）の合成）下記酸フルオライド（ＰＣＲ社製）１２．５ｇとエーテル５０ｍｌの混合物（２層分離）に、氷冷下で撹拌しながら２０ｍｌの水を滴下した。滴下中、一旦均一溶液となり、その後再び２層分離した。

【化６】

$$FOC-\underset{CF_3}{\underset{|}{C}}F-(OCF_2\underset{CF_3}{\underset{|}{C}}F)_{4\text{-}7}-OCF_2CF_2CF_3$$

【００２４】滴下終了後、３時間撹拌を続けた後、分液し、水相は３回エーテルで抽出した。エーテル相を集め、飽和食塩水で２回洗浄した後、エーテルを留去して無色の油状物１２．６ｇを得た。ＮＭＲ，ＩＲスペクト※ルから下記式（３）のカルボン酸を含む含フッ素エーテル化合物であることを確認した。

【化７】

$$HOOC-\underset{CF_3}{\underset{|}{C}}F-(OCF_2\underset{CF_3}{\underset{|}{C}}F)_n-OCF_2CF_2CF_3 \quad (3)$$

$$n \fallingdotseq 5$$

【００２５】（酸素ガス透過性の測定）交換容量９５０ｇ／当量のパーフルオロスルホン酸ポリマー（アシプレックス－Ｓ、旭化成工業（株）製）を、５重量%の濃度でｎ－プロパノールと２，２，３，３，３－ペンタフルオロプロパノールの混合溶媒（重量比１：１）に溶解した溶液に、上記式（３）の含フッ素エーテル化合物を、ポリマーとエーテル化合物との重量比が８：２となるように添加し、均一溶液とした。この溶液をシャーレに展開し、風乾した後、８０℃で真空乾燥して膜厚４２μｍのフィルムを作製した。このフィルムを水に浸漬した後、表面の水を拭き取り、フロー式ガス透過率測定システム（ＹＡＮＡＣＯ製、ＧＴＲ－１００ＦＡ）を用いて酸素ガス透過率を測定した。その結果、テストガスを加湿空気、セル温度を４０℃としたときの酸素ガス透過係数は5.0×10^{-9} cc・cm/cm²・sec・cmHgであった。比較のために上記含フッ素エーテル化合物を加えずに作製した、パーフルオロスルホン酸ポリマーのみのフィルムでの測定値は、2.5×10^{-9} cc・cm/cm²・sec・cmHgであった。

【００２６】（膜／電極接合体の作製）４０重量%の白金触媒担持カーボン（米国Ｅ－ＴＥＫ社製）に、上記溶液を、白金触媒とポリマー＋含フッ素エーテル化合物との重量比が２：１となるように添加し、均一に分散させてペーストを調製した。このペーストを２００メッシュのスクリーンを用いて、触媒面積２ｃｍ×２ｃｍとなるようにテフロンシート上に塗布した後、大気雰囲気中１００℃で乾燥・固定化し、白金担持量０．２５ｍｇ／ｃｍ²の触媒シートを得た。２枚の触媒シートの触媒層を向かい合わせ、その間に交換容量９５０ｇ／当量、厚さ１００μｍ、膜面積３ｃｍ×３ｃｍのパーフルオロスルホン酸ポリマー膜（アシプレックス－Ｓ１００４、旭化成工業（株）製）をはさみ、１５０℃、圧力５０ｋｇ／ｃｍ²でホットプレスした後、両面のテフロンシートを剥がし、膜／電極接合体を作製した。

【００２７】触媒層支持体として、厚さ約４００μｍのカーボンクロス（Ｅ－ＴＥＫ社製）を用い、テフロン分散液（６０重量%）に浸漬した後、３４０℃でシンタリングを行い、カーボンクロスに対し４０重量%含浸させた。その空隙率は５０％であった。これら膜／電極接合体と触媒層支持体とを積層し、燃料電池単セル評価装置に組み込み、燃料に水素ガス、酸化剤に空気を用い、常圧、セル温度８０℃で単セル特性試験を行った。水素ガスは９０℃で加湿を行い、空気は加湿せずそのままセルへ供給した。その結果、０．５、１．０Ａ／ｃｍ²の電流密度のときのセル出力電圧はそれぞれ０．６５Ｖ、０．５０Ｖであった。

【００２８】〈実施例２〉パーフルオロスルホン酸ポリマーと上記式（３）の含フッ素エーテル化合物との混合溶液において、ポリマーとエーテル化合物との重量比を６：４とした以外、実施例１と同様にフィルムを作製して酸素ガス透過性を測定したところ、酸素ガス透過係数は6.5×10^{-9} cc・cm/cm²・sec・cmHgであった。また、該組成物の溶液を用いて膜／電極接合体を作製し、単セル特性試験を行ったところ、０．５、１．０Ａ

／ｃｍ^2 の電流密度のときのセル出力電圧はそれぞれ０．６６Ｖ、０．５７Ｖであった。

【００２９】〈実施例３〉

（含フッ素エーテル化合物（５）の合成）耐圧容器中で無水硫酸（SO_3）とテトラフルオロエチレンを混合させた後、生成物を蒸留（沸点４２℃）して２－ヒドロキシテトラフロオロエタンスルホン酸スルトンを得た。この２－ヒドロキシテトラフルオロエタンスルホン酸スルトンを氷冷した状態で少量のトリエチルアミンを添加して開環させ、フルオロスルホニルジフルオロアセチルフルオライド（$FOCCF_2SO_2F$）を合成した。次に、耐圧容器にフルオロスルホニルジフルオロアセチルフルオライド５０ｇと乾燥フッ化セシウム６．０ｇと乾燥ジグライム５０ｍｌとを入れ、氷冷下、ヘキサフルオロプロピレンオキサイド約３８０ｇを数回に分けて圧入した。そのまま０℃で８時間反応させ、沸点～１００℃／３ｍｍＨｇの成分３２ｇを得た。生成物の一部をメタノールと反応させて得られたメチルエステルのＮＭＲ，ＩＲスペクトルから下記式（４）の化合物であることを確認した。

【化８】

$$FOC-\underset{\textstyle CF_3}{CF}-(OCF_2\underset{\textstyle CF_3}{CF})n-OCF_2CF_2SO_2F \qquad (4) \qquad n≒4$$

【００３０】上記化合物（４）５．０ｇに対し、４０％ＮａＯＨ水溶液５ｇを加えて１００℃で５時間攪拌し、引き続き１９０℃で５時間攪拌した。室温まで冷却後、３５％硫酸で酸性にしてエーテルで抽出した。エーテル相を濃縮して淡褐色の油状物３．２ｇを得た。ＮＭＲ，ＩＲスペクトルから下記式（５）の含フッ素エーテル化合物であることを確認した。ｎの値はＮＭＲで再度確認した。

【化９】

$$CF_2CHF-(OCF_2\underset{\textstyle CF_3}{CF})n-OCF_2CF_2SO_3H \qquad (5) \qquad n≒4$$

【００３１】（酸素ガス透過性の測定及び膜／電極接合体の作製）含フッ素エーテル化合物として上記式（５）の化合物を用いた以外、実施例１と同様にフィルムを作製して酸素ガス透過性を測定したところ、酸素ガス透過係数は５．７×１０$^{-9}$cc・cm/cm^2・sec・cmHgであった。また、該組成物の溶液を用いて膜／電極接合体を作製し、単セル特性試験を行ったところ、０．５、１．０Ａ／ｃｍ^2 の電流密度のときのセル出力電圧はそれぞれ０．６８Ｖ、０．５４Ｖであった。

【００３２】〈実施例４〉パーフルオロスルホン酸ポリマーと上記式（５）の含フッ素エーテル化合物との混合溶液において、ポリマーとエーテル化合物との重量比を６：４とした以外、実施例３と同様にフィルムを作製して酸素ガス透過性を測定したところ、酸素ガス透過係数は１．９×１０$^{-8}$cc・cm/cm^2・sec・cmHgであった。また、該組成物の溶液を用いて膜／電極接合体を作製し、単セル特性試験を行ったところ、０．５、１．０Ａ／ｃｍ^2 の電流密度のときのセル出力電圧はそれぞれ０．６９Ｖ、０．５８Ｖであった。

【００３３】〈実施例５〉

（含フッ素エーテル化合物（６）の合成）実施例３で合成した上記式（４）の化合物５．０ｇを１０ｍｌのパーフルオロヘキサンに溶かしておき、４０％ＮａＯＨ水溶液５ｇを加えて室温で１時間攪拌した後、還流温度（６５℃）で５時間攪拌した。室温まで冷却後、濾過して得られた白色固体をエタノールに溶かし、不溶物を濾過して除き、濾液を濃縮して白色粉末を得た。得られた粉末を３５％硫酸で酸性にしてエーテルで抽出し、エーテル相を濃縮して淡褐色の油状物２．９ｇを得た。ＮＭＲ，ＩＲスペクトルから下記式（６）の含フッ素エーテル化合物であることを確認した。

【化１０】

$$HOOC-\underset{\textstyle CF_3}{CF}-(OCF_2\underset{\textstyle CF_3}{CF})n-OCF_2CF_2SO_3H \qquad (6) \qquad n≒4$$

【００３４】（酸素ガス透過性の測定及び膜／電極接合体の作製）含フッ素エーテル化合物として上記式（６）の化合物を用いた以外、実施例１と同様にフィルムを作製して酸素ガス透過性を測定したところ、酸素ガス透過係数は５．８×１０$^{-9}$cc・cm/cm^2・sec・cmHgであった。また、該組成物の溶液を用いて膜／電極接合体を作製し、単セル特性試験を行ったところ、０．５、１．０Ａ／ｃｍ^2 の電流密度のときのセル出力電圧はそれぞれ０．６８Ｖ、０．５５Ｖであった。

【００３５】〈実施例６〉パーフルオロスルホン酸ポリマーと上記式（６）の含フッ素エーテル化合物との混合溶液において、ポリマーとエーテル化合物との重量比を６：４とした以外、実施例５と同様にフィルムを作製して酸素ガス透過性を測定したところ、酸素ガス透過係数は２．７×１０$^{-8}$cc・cm/cm^2・sec・cmHgであった。また、該組成物の溶液を用いて膜／電極接合体を作製し、単セル特性試験を行ったところ、０．５、１．０Ａ／ｃｍ^2 の電流密度のときのセル出力電圧はそれぞれ０．７

０Ｖ、０．５９Ｖであった。

【００３６】〈実施例７〉

（含フッ素エーテル化合物（７）の合成）実施例３で合成した上記式（４）の化合物１０ｇを、直前に１８０℃で真空乾燥した炭酸カリウム１０ｇに滴下した後、１３０℃で２時間加熱し、さらに１９０℃で２時間加熱した。室温まで冷却後、水を加え、さらにエーテルで抽出し、エーテルを留去後、得られた油状物を２０ｍｌのパーフルオロヘキサンに溶かしておき、４０％ＮａＯＨ水＊溶液１０ｇを加えて室温で１時間攪拌した後、還流温度（６５℃）で５時間攪拌した。室温まで冷却後、濾過して得られた白色固体をエタノールに溶かし、不溶物を濾過して除き、濾液を濃縮して白色粉末を得た。得られた粉末を３５％硫酸で酸性にしてエーテルで抽出し、エーテル相を濃縮して淡褐色の油状物４．５ｇを得た。ＮＭＲ，ＩＲスペクトルから下記式（７）の含フッ素エーテル化合物であることを確認した。

【化１１】

$$CF_2=CF-(OCF_2\underset{\displaystyle CF_3}{\underset{|}{C}}F)n-OCF_2CF_2SO_3H \qquad (7)$$

$$n \fallingdotseq 4$$

【００３７】（酸素ガス透過性の測定及び膜／電極接合体の作製）含フッ素エーテル化合物として上記式（７）の化合物を用いた以外、実施例２と同様にフィルムを作製して酸素ガス透過性を測定したところ、酸素ガス透過係数は1.2×10^{-8}cc・cm/cm^2・sec・cmHgであった。また、該組成物の溶液を用いて膜／電極接合体を作製し、単セル特性試験を行ったところ、０．５、１．０Ａ／ｃｍ^{2}の電流密度のときのセル出力電圧はそれぞれ０．６８Ｖ、０．５７Ｖであった。※

※【００３８】〈実施例８〉

（含フッ素エーテル化合物（８）の合成）実施例７で合成した上記式（７）の化合物２．０ｇを１０ｍｌの四塩化炭素に溶かしておき、室温で塩素ガスを吹き込んだ。反応後、溶媒を留去して淡褐色の油状物２．２ｇを得た。ＮＭＲ，ＩＲスペクトルから下記式（８）の含フッ素エーテル化合物であることを確認した。

【化１２】

$$CClF_2CClF-(OCF_2\underset{\displaystyle CF_3}{\underset{|}{C}}F)n-OCF_2CF_2SO_3H \qquad (8)$$

$$n \fallingdotseq 4$$

【００３９】（酸素ガス透過性の測定及び膜／電極接合体の作製）含フッ素エーテル化合物として上記式（８）の化合物を用いた以外、実施例２と同様にフィルムを作製して酸素ガス透過性を測定したところ、酸素ガス透過係数は1.7×10^{-8}cc・cm/cm^2・sec・cmHgであった。また、該組成物の溶液を用いて膜／電極接合体を作製し、単セル特性試験を行ったところ、０．５、１．０Ａ／ｃｍ^{2}の電流密度のときのセル出力電圧はそれぞれ０．６９Ｖ、０．５８Ｖであった。

【００４０】〈比較例１〉含フッ素エーテル化合物を添加しない以外は実施例１と同様に膜／電極接合体を作製し、単セル特性試験を行った。その結果、０．５、１．０Ａ／ｃｍ^{2}の電流密度のときのセル出力電圧はそれぞれ０．６０Ｖ、０．４４Ｖであった。

【００４１】

【発明の効果】本発明の電極触媒被覆剤は固体高分子型燃料電池のガス拡散電極に用いた場合、酸化剤として空気を用いたときに、従来材料に比べて高い出力電圧が得られる。従って、本発明の電極触媒被覆剤を用いた膜／電極接合体もまた従来のものに比べて優れている。